PB89-142723

Atmospheric Wet Sulphate Deposition and Lakewater Chemistry (Journal Version)

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Feb 88

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1. REPORT NO. EPA/600/J-88/235	2.
3. PB89-142723	
4. TITLE AND SUBTITLE Atmospheric wet sulphate deposition and lakewater chemistry (Journal Version)	5. REPORT DATE 1988
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T.J. Sullivan, J.M. Eilers, M.R. Church, D.J. Blick, K.N. Eshleman, D.H. Landers and M.S. DeHaan	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS USEPA, Corvallis, OR	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency Environmental Research Laboratory 200 SW 35th Street Corvallis, OR 97333	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/2

15. SUPPLEMENTARY NOTES Nature, Vol. 331, No. 6157, pp. 607-609, 18 February 1988

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 4
	20. SECURITY CLASS (This page) Unclassified	22. PRICE A02

EPA Form 2220-1 (9-73)

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EPA/600/J-88/235
JOURNAL ARTICLE

Atmospheric wet sulphate deposition and lakewater chemistry

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Atmospheric sulphur deposition and its impacts on surface-water chemistry and biota have been extensively studied in several areas of the United States and elsewhere during the past two decades[1,2]. In the absence of regionally based statistical (probability) sampling, however, it has not been possible to extrapolate the results from intensive small-scale studies to a regional population. Here we present data from the first regional probability sampling of lakes in the United States[3,4], indicating that median lake sulphate concentrations correlate highly with estimated wet sulphate deposition at lake sites. The data further suggest that acid deposition has depleted acid-neutralizing capacity (ANC) in low-base-cation lakes, and that some high-base-cation lakes receive substantial sulphate from internal watershed sources. Data suggest that acidic lakes greater than 4 hectares in surface area are generally not found in areas receiving low sulphate deposition, whereas most acidic lakes in the northeastern United States are currently acidic because of high sulphate relative to base cation concentrations.

Lake chemistry data were taken from the recent National Lake Survey (NLS)[3,4], conducted by the US Environmental Protection Agency (EPA). Details on statistical design, sampling, analytical methodologies, and quality assurance protocols were provided by Linthurst *et al.*[3] and Landers *et al.*[4]. Estimates of wet SO_4^{2-} deposition at each lake site were derived from interpolated precipitation volume and chemistry data. For the northeastern USA, precipitation volumes were obtained from 30-year precipitation norm values, 1951–80, for 500 stations (National Climate Center, NOAA), and precipitation chemistry data were derived from NADP/NTN estimates for the 1-year period before lake sampling. In the upper midwestern and southeastern USA, interpolations based on precipitation volumes were not available for the long term. We therefore used interpolations from 3 years of precipitation volume and chemistry data from 162 stations in the Acid Deposition System, 1980–82 (ref. 5). Deposition estimates were assigned by interpolating both SO_4^{2-} concentration and precipitation volumes. Because of the sparse monitoring of precipitation chemistry and volume in the western United States, an SO_4^{2-} deposition value was derived from 1981–84 annual averages for one or more NADP/NTN sites considered most appropriate for the lake study areas, rather than interpolating to each site[6]. Lake chemistry data in the Northeast were corrected for estimated marine contributions of SO_4^{2-}, Cl^-, and base cations and estimated anthropogenic NaCl inputs. Marine Cl^- was estimated by using an empirical relation between Cl^- and distance to the coast from a data set of 'undisturbed' lakes, defined as those without paved roads in the watersheds based on examination of 1:250,000-scale US Geological Survey topographic maps. These estimated values for marine Cl^- were used for sea-salt corrections by assuming that the proportion of ions in the precipitation was the same as in seawater. Cl^- in excess of the marine estimate was assumed to have originated from anthropogenic sources, such as road salt, and was used to correct Na^+ values on an equivalent basis. Values adjusted by these procedures are designated by asterisks.

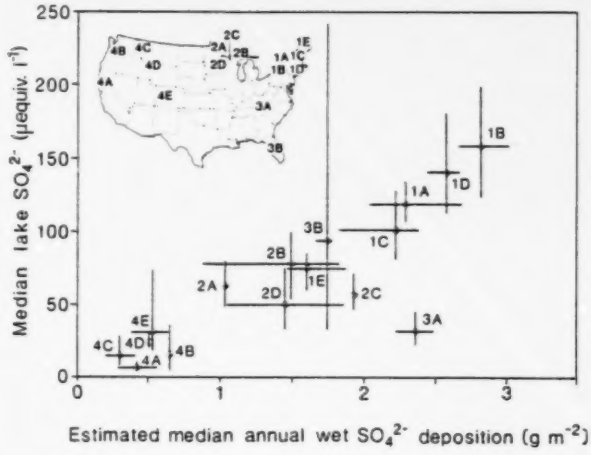

Fig. 1 Median (circle) and 25th and 75th percentiles (bars) of measured lake $[SO_4^{2-}]$ as a function of wet SO_4^{2-} deposition for subregions of the National Lake Survey. Deposition was estimated at each lake site for Eastern and Upper Midwestern lakes from interpolated precipitation volume and chemistry data. Estimated wet SO_4^{2-} deposition in the Western Region was taken from Hidy and Young[6]. Map insert depicts regions and subregions included in the EPA National Lake Survey. Subregion designations are as follows: 1A, Adirondacks; 1B, Poconos/Catskills; 1C, Central New England; 1D, Southern New England; 1E, Maine; 2A, Northeastern Minnesota; 2B, Upper Peninsula of Michigan; 2C, Northcentral Wisconsin ; 2D, Upper Great Lakes Area; 3A, Southern Blue Ridge; 3B, Florida; 4A, California; 4B, Pacific Northwest, 4C, Northern Rockies; 4D, Central Rockies; 4E, Southern Rockies. SO_4^{2-} values were not corrected for marine contributions.

Table 1 Lake chemistry from North American areas currently receiving low wet SO_4^{2-} deposition (generally <10 kg ha^{-1} yr^{-1})

		Median				Percentage of lakes ≤ANC criterion		
Subregion*	n†	pH	ANC	SO_4^{2-} (μequiv. l^{-1})	A^-‡	0	20 (μequiv. l^{-1})	40
NW Ontario	1,078	7.1	254	75	94	0.002	<2	4
Labrador	182	6.4	46	24	47	0	15	43
NE Minnesota	150	6.9	185	62	89	0	0	2
California	150	6.9	63	7	10	0	8	27
Pacific NW	159	7.0	140	15	13	0	6	17
Northern Rocky Mts	143	7.4	195	16	12	0	<1	8
Central Rocky Mts	129	7.2	105	24	12	0.6§	1	4
Southern Rocky Mts	139	7.6	317	35	15	0	<1	3

* Canadian data from Jeffries *et al.*[9] and Jeffries (personal communication), Minnesota data from Linthurst *et al.*[3], Western subregions from Landers *et al.*[4]. All summary statistics presented above, except data from Canada, are population estimates.

† n = number of lakes with measured ANC.

‡ A^- (organic anion concentration) estimated using method described by Oliver *et al.*[17].

§ One naturally acidic lake sampled in Yellowstone National Park, influenced by a hot spring.

ANC was defined from charge-balance considerations as $\sum$ strong-base cations (C_B) $-\sum$ strong-acid anions (C_A):

$$ANC = [Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}] - [SO_4^{2-} + NO_3^{-} + Cl^{-} + A_s^{-}] \quad (1)$$

where A_s^- refers to strong organic acid anion (all concentrations in μequiv. l^{-1}). We define 'acidic' lakes as those with measured (modified Gran analysis) ANC ≤ 0.

When expressed as median values for each subregion, lakewater $[SO_4^{2-}]$ was highly correlated with estimated wet SO_4^{2-} deposition for each subregion (Fig. 1). Several processes can modify surface water $[SO_4^{2-}]$ relative to input. In addition, dry deposition of sulphur, which was not estimated because regional data are not yet available, can significantly alter the total sulphur input relative to measured wet deposition. It is therefore not surprising that scatter exists in a plot of lake $[SO_4^{2-}]$ against wet deposition. In spite of these uncertainties, however, lake sulphate concentrations in the western, upper midwestern and northeastern United States and Florida exhibit an approximately linear relation with increasing wet deposition. The Southern Blue Ridge subregion appears to be an outlier, supporting the observation that net sulphur retention (principally sulphate adsorption in soils) is high in many southeastern systems[7,8]. The high variability of lake $[SO_4^{2-}]$ in Florida reflects the heterogeneity of lakes in this subregion. Extremely high sulphate concentrations in many Florida lakes appear to be associated with an influx of sulphur-rich groundwater from the Floridan aquifer[3].

We did not find an obvious relationship between lake $[SO_4^*]$ and ANC for the full regional or subregional data sets, in agreement with analyses of data from eastern Canada[9]. This is because $[SO_4^*]$ is expected to correlate with loss of ANC, rather than ANC *per se*. $[Ca^* + Mg^*]$ provides a better estimate of original lake susceptibility to acidic deposition effects than does ANC for low-base-cation lakes[10]. We therefore stratified northeastern lakes into five $[Ca^* + Mg^*]$ strata. A statistically significant ($P < 0.001$) negative relationship was found between lake $[SO_4^*]$ and ANC within each of the four lowest $[Ca^* + Mg^*]$ strata (Fig. 2). Multiple regression analysis of measured ANC as a function of $[Ca^*]$, $[Mg^*]$, and $[SO_4^*]$ yielded the following equation for lakes in the north-east:

$$ANC = 23.86 + 1.02[Ca^*] + 0.94[Mg^*] - 0.96[SO_4^*] \quad (R^2 = 0.98,\ n = 759) \quad (2)$$

Subregionally, results yielded comparable parameter estimates, with R^2 ranging from 0.91 (southern New England) to 0.99 (Adirondacks and central New England). The observed good fit reconfirmed our charge-balance definition of ANC presented in equation (1) (ignoring Na^+, K^+, NO_3^-, Cl^-, A_s^- and marine inputs of Ca^{2+}, Mg^{2+} and SO_4^{2-}). These results are illustrative of the negative relationship between $[SO_4^*]$ and ANC in northeastern lakes, when $[Ca^*]$ and $[Mg^*]$ are also taken into account.

A small number of lakes had very high $[SO_4^*]$, probably derived from watershed sources. This theory was tested by examining the ratio of $[SO_4^{2-}]$ in lakewater to $[SO_4^{2-}]$ in precipitation, using volume-weighted mean precipitation chemistry values interpolated to each lake site from NADP/NTN data for the 1-year period before lake sampling. Removal of SO_4^{2-} is thought to be low for northeastern lakes from SO_4^{2-} adsorption in watershed soils[7,8] and microbial SO_4^{2-} reduction[11] in these primarily drainage systems. Thus, if dry deposition may be slightly in excess of wet deposition[12] and the evapoconcentration factor is near two[13], we expect lake SO_4^{2-} : precipitation SO_4^{2-} ratios to have an upper bound of ~4:1 to 5:1, although a definitive bound cannot be established. For northeastern lakes included in this study having $[Ca^* + Mg^*] \leq 200$ μequiv. l^{-1}, this ratio was generally within the expected range (mean ± 2 s.d. = 2.92 ± 1.60). Many lakes with high base cation concentrations ($[Ca^* + Mg^*] > 200$ μequiv. l^{-1}) exhibited lake SO_4^{2-} enrichment considerably higher than expected (4.29 ± 4.98). For lakes with low base cation concentrations ($[Ca^* + Mg^*] \leq 200$ μequiv. l^{-1}), 2.1% of the population had a ratio exceeding 5.0, and 0.2% exceeding 6.0. For lakes with higher base cation concentrations, however, many more lakes exceeded these criteria, 23.1% and 13.7%, respectively. It appears that internal sources of SO_4^{2-} are significant for many of the lakes with high base cation and ANC concentrations. Although internal sources of SO_4^{2-} cannot be ruled out for lakes with low base cation concentrations, we observed no evidence that such sources are substantial.

Table 1 gives recent lake chemistry distributions from areas of North America currently receiving low wet deposition of SO_4^{2-} (generally <10 kg ha^{-1} yr^{-1}). Despite widely varying ANC (median 46 to 317 μequiv. l^{-1}), estimated organic anion concentrations (median 10 to 94 μequiv. l^{-1}), geology, soils and vegetation, all subregions were remarkably similar in that they had few or no acidic lakes. Although several acidic lakes with high dissolved organic carbon were sampled in the Okefenokee Swamp of Georgia[3], it appears that, on a regional basis, in temperate glaciated terrain, acidic lakes are generally absent in areas with low SO_4^{2-} deposition. We emphasize, however, that small lakes (especially those <4 ha and to a lesser extent, those from 4 to 10 ha) are under-represented in the data from Canada and Minnesota (Table 1). Note also that the two pristine subregions containing the highest estimated organic anion concentrations (Northwest Ontario and Northeast Minnesota, 94 and

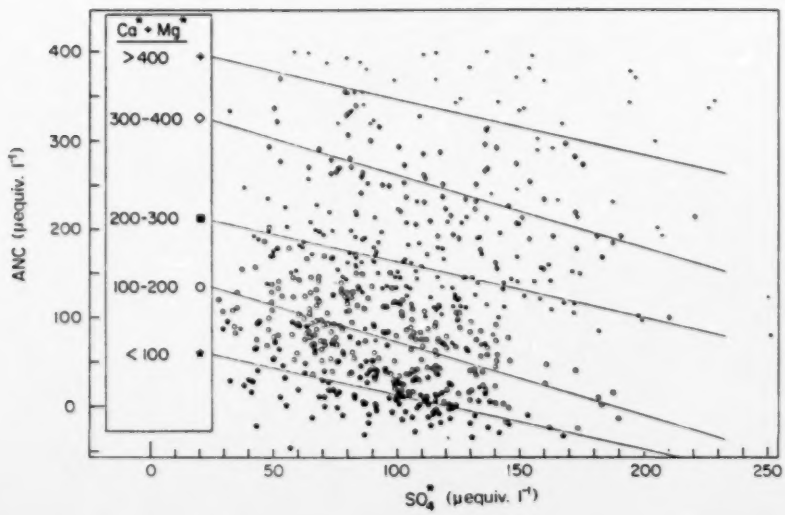

Fig. 2 Measured ANC plotted against nonmarine sulphate for northeastern lakes having ANC ≤ 400 μequiv. l^{-1}. Lakes are stratified according to $[Ca^* + Mg^*]$, and 15 lakes having $SO_4^* > 250$ μequiv. l^{-1} were deleted. Best-fit linear regression lines are provided to indicate relative slope, but regression equations are not provided because they should not be used for predictive purposes.

89 μequiv. l^{-1}, respectively) also had low percentages of low-ANC lakes. Only 4% and 2%, respectively, of the lakes in these subregions had ANC ≤ 40 μequiv. l^{-1}.

Recognizing the inherent limitations of interregional comparisons because of differences in physical characteristics and deposition history, the data in Table 1 suggest that acidic northeastern lakes >4 ha would likely not be acidic in the absence of SO_4^*. This contention can be further examined on the basis of the SO_4^*/C_B^* ion ratio in acidic NLS lakes. From the charge balance definition of ANC (equation (1)), it follows that if SO_4^* exceeds C_B^*, then lakewater will be acidic. Of the northeastern lakes measured as acidic (population estimate, $\hat{N} = 326$), 85% also had a ratio of $SO_4^*/C_B^* > 1$. This suggests that these lakes are now acidic due to SO_4^*.

It is evident that most northeastern lakes that now have ANC ≤ 0 μequiv. l^{-1} are acidic because of SO_4^*. It is not clear, however, whether some of these lakes may previously have been acidic from another source, such as organic acids[14,15]. But available data from low-deposition areas in North America (Table 1) suggest that, for the lakes considered (that is, those generally >4 ha), temperate North American lakes are not acidic in the absence of anthropogenic sulphate. Palaeolimnological investigations of diatom remains in lake sediments have suggested that many northeastern lakes were acidic in pre-industrial times, but these have almost exclusively been small lakes (<10 ha)[16].

We thank B. Rochelle, Roze Royce and R. Sauter for assistance; S. Christie, A. Henriksen, D. Johnson, E. Krug, D. McKenzie, H. Seip and P. Shaffer for valuable criticisms; A. Olsen and R. Olson for interpolating wet deposition chemistry to NLS sites; and D. Brown for lake disturbance classification. The research described here was funded as part of the National Acid Precipitation Assessment Program by the EPA. This paper was prepared at the EPA's Research Laboratory in Corvallis, Oregon, in part through Contract 68-03-3246 with Northrop Services, and is a contribution from EPA's Aquatic Effects Research Program. It has been subjected to the agency's peer and administrative review and approved for publication.

Received 27 August; accepted 17 November 1987.

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